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(21) International Application Number: PCT/US97/19899 (22) International Filing Date: 3 November 1997 (03.11.97) (30) Priority Data: 60/030,757 1 November 1996 (01.11.96) US (71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors: DE-CERDA, Luisa Navarro; Urb. Monterrey Calle A Las Cimas Town House Letra D, La Trinidad Caracas (VE). PRADA-SILVY, Ricardo Alfredo; Ur- banizacion Cumbres de Curumo, Caracas 1080 (VE). MASSEY-BROOKER, Anju, Deepali; 41 Polwarth Road, Brunton Park, Gosforth, Newcastle upon Tyne NE3 5NE (GB). GUEDIRA, Nour-Eddine; 115D Osborne Road, Jesmond, Newcastle upon Tyne NE2 2TA (GB). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: BR, CA, CN, MX. Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: HAND WASH LAUNDRY DETERGENT COMPOSITIONS CONTAINING A COMBINATION OF SURFACTANTS AND SOIL RELEASE POLYMER		
(57) Abstract <p>The subject invention involves laundry detergent compositions, preferably in granular form, particularly useful for machine laundry operations. The compositions comprise: a) from about 6 % to about 18 % surfactant comprising 1) from about 5 % to about 10 % anionic surfactant selected from alkylbenzene sulfonate surfactant, alkyl sulfate surfactant and alkyl ethoxy ether sulfate surfactant; 2) from about 0.2 % to about 4 % hydroxyalkyl quaternary ammonium cationic surfactant; and 3) from 0.4 % to about 8 % nonionic surfactant selected from alkyl ethoxy alcohol surfactant, amine oxide surfactant, and polyhydroxy fatty acid amide surfactant; b) from about 0.05 to about 4 % polymeric soil release agent comprising: 1) from about 10 % to about 99.5 % esters comprising, per mole of said ester: i) from about 1 to about 2 moles of sulfonated polyethoxy/propoxy end-capping units; ii) from about 0.5 to about 66 moles of units selected from the group consisting of a) oxyethyleneoxy units; b) a mixture of oxyethyleneoxy and oxy-1,2-propyleneoxy units; and c) a mixture of a) or b) with poly(oxyethylene)oxy units; iii) from about 1.5 to about 40 moles of terephthaloyl units; and iv) from 0 to about 26 moles of 5-sulfoisophthaloyl units; 2) from about 0.5 % to about 20 % crystallization-reducing stabilizer selected from sulfonate-type hydrotrope, alkylbenzene sulfonate, paraffin sulfonate, and mixtures thereof; and c) from about 80 % to about 94 % other components.</p>		

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HAND WASH LAUNDRY DETERGENT COMPOSITIONS CONTAINING A COMBINATION OF SURFACTANTS AND SOIL RELEASE POLYMER

TECHNICAL FIELD

The subject invention involves laundry detergent compositions containing a certain mixture of surfactants and soil release polymer.

BACKGROUND OF THE INVENTION

Throughout the world, many people clean fabrics by machine washing with compositions containing soap and/or detergent. Products which provide improved cleaning of fabrics are continually being sought.

It is an object of the subject invention to provide detergent laundry compositions which provide superior cleaning performance in machine wash laundry operations.

SUMMARY OF THE INVENTION

The subject invention involves laundry detergent compositions, preferably in granular form, comprising:

- a) from about 6% to about 18% surfactant comprising:
 - 1) from about 5% to about 10% anionic surfactant selected from alkylbenzene sulfonate surfactant, alkyl sulfate surfactant and alkyl ethoxy ether sulfate surfactant having an average of from about 0.5 to about 9 moles ethoxy per mole surfactant;
 - 2) from about 0.2% to about 2% hydroxyalkyl quaternary ammonium cationic surfactant having the structure:



wherein R is long-chain alkyl, R' is short-chain alkyl, R'' is $H(OCH_2CHB)_p$, B is H or CH_3 , n is 0 to 3, m is 0 to 3, n + m is 3, p is from about 0.5 to about 4, p times m is from about 0.5 to about 4, and Z^- is a water-soluble anion; and

- 3) from 0.4% to about 8% nonionic surfactant selected from alkyl ethoxy alcohol surfactant having an average of from about 0.5

to about 25 moles ethoxy per mole surfactant, amine oxide surfactant, and polyhydroxy fatty acid amide surfactant;

- b) from about 0.05 to about 4% polymeric soil release agent comprising:
 - 1) from about 10% to about 99.5% esters comprising, per mole of said ester:
 - i) from about 1 to about 2 moles of sulfonated poly-ethoxy/propoxy end-capping units of the formula $(\text{MO}_3\text{S})(\text{CH}_2)_m(\text{CH}_2\text{CH}_2\text{O})(\text{RO})_n$ wherein M is a salt-forming cation such as sodium or tetraalkylammonium, m is 0 or 1, R is ethylene, propylene or a mixture thereof, and n is from 0 to 2; and mixtures thereof;
 - ii) from about 0.5 to about 66 moles of units selected from the group consisting of:
 - a) oxyethyleneoxy units;
 - b) a mixture of oxyethyleneoxy and oxy-1,2-propyleneoxy units having an oxyethyleneoxy to oxy-1,2-propyleneoxy mole ratio ranging from 0.5:1 to about 10:1; and
 - c) a mixture of a) or b) with poly(oxyethylene)oxy units wherein said poly(oxyethylene)oxy units have a degree of polymerization of from 2 to 4; provided that when said poly(oxyethylene)oxy units have a degree of polymerization of 2, the mole ratio of poly(oxyethylene)oxy units to total group ii) units ranges from 0:1 to about 0.33:1; and when said poly(oxyethylene)oxy units have a degree of polymerization of 3, the mole ratio of poly(oxyethylene)oxy units to total group ii) units ranges from 0:1 to about 0.22:1; and when said poly(oxyethylene)oxy units have a degree of polymerization of 4, the mole ratio of poly(oxyethylene)oxy units to total group ii) units ranges from 0:1 to about 0.14:1;
 - iii) from about 1.5 to about 40 moles of terephthaloyl units; and
 - iv) from 0 to about 26 moles of 5-sulfoisophthaloyl units of the formula $-(\text{O})\text{C}(\text{C}_6\text{H}_3)(\text{SO}_3\text{M})\text{C}(\text{O})-$ wherein M is a salt

forming cation such as an alkali metal or tetraalkylammonium ion;

- 2) from about 0.5% to about 20% crystallization-reducing stabilizer selected from sulfonate-type hydrotrope, alkylbenzene sulfonate, paraffin sulfonate, and mixtures thereof; and
- c) from about 80% to about 94% other components.

DETAILED DESCRIPTION OF THE INVENTION

All percentages used herein are weight percent unless otherwise specified.

As used herein, the term "alkyl" means a hydrocarbyl moiety which is straight (linear) or branched, saturated or unsaturated. Unless otherwise specified, alkyl are preferably saturated ("alkanyl") or unsaturated with double bonds ("alkenyl"), preferably with one or two double bonds. As used herein "long-chain alkyl" means alkyl having about 8 or more carbon atoms, and "short-chain alkyl" means alkyl having about 3 or fewer carbon atoms.

The term "tallow" is used herein in connection with materials having alkyl mixtures derived from fatty acid mixtures from tallow which typically are linear and have an approximate carbon chain length distribution of 2% C₁₄, 29% C₁₆, 23% C₁₈, 2% palmitoleic, 41% oleic, and 3% linoleic (the first three listed being saturated). Other mixtures with similar alkyl distribution, such as those from palm oil and those derived from various animal tallows and lard, are also included within the term tallow. The tallow, as used herein, can also be hardened (i.e., hydrogenated) to convert part or all of the unsaturated alkyl moieties to saturated alkyl moieties.

The term "coconut" is used herein in connection with materials having alkyl mixtures derived from fatty acid mixtures from coconut oil which typically are linear and have an approximate carbon chain length distribution of about 8% C₈, 7% C₁₀, 48% C₁₂, 17% C₁₄, 9% C₁₆, 2% C₁₈, 7% oleic, and 2% linoleic (the first six listed being saturated). Other mixtures with similar alkyl distribution, such as palm kernel oil and babassu oil, are included within the term coconut.

Compositions of the subject invention are preferably in solid, granular form, although other forms of laundry detergents are also included.

Surfactants

Compositions of the subject invention comprise from about 6% to about 18% surfactant, preferably from about 8% to about 15% surfactant, more preferably from about 10% to about 14% surfactant, more preferably still from about 11% to about 13% surfactant.

As used herein, "alkylbenzene sulfonate" surfactant means a salt of alkylbenzene sulfonic acid with an alkyl portion which is linear or branched, preferably having an average chain length of from about 9 to about 16 carbon atoms, more preferably from about 11 to about 14 carbon atoms. The alkyl are preferably saturated. Branched or mixed branched and linear alkylbenzene sulfonate is known as ABS. Linear alkylbenzene sulfonate, known as LAS, is more biodegradable than ABS, and is preferred for the subject invention compositions. The acid forms of ABS and LAS are referred to herein as HABS and HLAS, respectively. Alkylbenzene sulfonates and processes for making them are disclosed in U.S. Patent Nos. 2,220,099 and 2,477,383, incorporated herein by reference.

The salts of the alkylbenzene sulfonic acid are preferably the alkali metal salts, such as sodium and potassium, especially sodium. Salts of alkylbenzene sulfonic acid also include magnesium and ammonium. A particularly preferred LAS surfactant has saturated linear alkyl with an average of 11.5 to 12.5 carbon atoms, and is a sodium salt ($C_{11.5}C_{12.5}LAS \cdot Na$).

As used herein, "alkyl sulfate surfactant" or "AS" includes the salts of alkyl sulfuric acid, with a long-chain alkyl, linear or branched, preferably linear, preferably having an average chain length from about 10 to about 16 carbon atoms, more preferably from about 12 to about 15 carbon atoms. Especially preferred is alkyl sulfate made by sulfating primary alcohol derived from coconut or tallow and mixtures thereof. Salts of alkyl sulfate include sodium, potassium, lithium, ammonium, and alkylammonium salts. Preferred salts of alkyl sulfate are sodium and potassium salts, especially sodium.

As used herein, "alkyl ethoxy ether sulfate surfactant" or "AES" has the following structure: $R''O(C_2H_4O)_xSO_3M$. R'' is long-chain alkyl preferably having an average of from about 10 to about 16, more preferably from about 12 to about 15, carbon atoms. R'' is preferably saturated. R'' is preferably linear. The "degree of ethoxylation" (number of moles of ethoxy per mole of surfactant) is represented by x , and is, on average, from about 0.5 to about 9, preferably from about 1 to about 7, more preferably from about 2 to about 5, especially about 3. M is a water-soluble cation, for example, an alkali metal cation (e.g., sodium, potassium, lithium), an alkaline earth metal cation (e.g., calcium, magnesium), ammonium or substituted-ammonium cation. M is preferably sodium or potassium, especially sodium.

The compositions of the subject invention comprise from about 5% to about 10% anionic surfactant selected from alkylbenzene sulfonate surfactant,

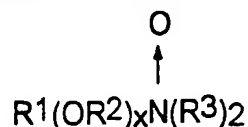
alkyl sulfate surfactant, and alkyl ethoxy ether surfactant; the subject compositions preferably comprise from about 6% to about 9%, more preferably from about 6.5% to about 8.5%, more preferably still from about 7% to about 8% such anionic surfactant. The anionic surfactant preferably comprises at least about 50%, more preferably at least about 80%, more preferably still about 100%, alkylbenzene sulfonate surfactant.

As used herein, "hydroxyalkyl quaternary ammonium cationic surfactant" or "HAQA" means a surfactant having the following structure: $R R'_n R''_m N^+ Z^-$. R is a long-chain alkyl, linear or branched, preferably having an average of from about 9 to about 16, more preferably from about 12 to about 14, carbon atoms. R is preferably saturated. R is preferably linear. R' is a short-chain alkyl having from 1 to about 3 carbon atoms; R' is preferably methyl or ethyl, especially methyl. R'' is $H(OCH_2CHB)_p$; wherein B is H or CH_3 , preferably H; and p is on average from about 0.5 to about 4, preferably from about 0.8 to about 2, more preferably about 1. n is 0 to 3, preferably 1 or 2, more preferably 2. m is 0 to 3, preferably 1 or 2, more preferably 1. n + m is 3. p times m is from about 0.5 to about 4, preferably from about 0.8 to about 2, preferably about 1. Z^- is a water-soluble anion, such as halide, sulfate, methylsulfate, ethylsulfate, phosphate, hydroxide, fatty acid (laurate, myristate, palmitate, oleate, or stearate), or nitrate anion. Preferably Z^- is chloride, bromide or iodide, especially chloride.

The subject compositions comprises from about 0.2% to about 2% of HAQA cationic surfactant, preferably from about 0.3% to about 1.2%, more preferably less than about 1%, even more preferably from about 0.4% to about 0.8%, more preferably still from about 0.5% to about 0.7%.

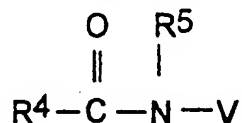
As used herein, "alkyl ethoxy alcohol nonionic surfactant" or "AE" means an ethoxylated fatty alcohol surfactant. Such surfactant preferably has a long-chain alkyl, preferably having an average of from about 9 to about 18, more preferably from about 12 to about 15 carbon atoms. The alkyl is preferably saturated. The alkyl is preferably linear. For the AE surfactant, the "degree of ethoxylation" (number of moles of ethoxy per mole of surfactant) is, on average, from about 0.5 to about 25, preferably from about 5 to about 12, more preferably from about 6 to about 10, especially about 7-9.

As used herein, "amine oxide surfactant" has the structure:



wherein R¹ is long-chain alkyl, preferably having an average of from about 10 to about 18, more preferably from about 12 to about 16, carbon atoms; R² is an alkylene or hydroxyalkylene containing from about 2 to about 3 carbon atoms; x is from 0 to about 3, preferably 0 or 1, more preferably 0; and each R³ is alkyl or hydroxyalkyl, preferably alkyl, having from about 1 to about 3, preferably 1, carbon atoms. Preferred amine oxide surfactants are alkyl dimethyl amine oxides.

As used herein, "polyhydroxy fatty acid amide surfactant" has the formula:



wherein R⁴ is long-chain alkyl, preferably having an average of from about 10 to about 18, more preferably from about 12 to about 16, carbon atoms; R⁵ is about C₁-C₆ alkyl, hydroxyalkyl, or alkyloxyalkyl, preferably methyl; and V is a polyhydroxyhydrocarbyl moiety preferably derived from a reducing sugar. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials for making such surfactant, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for V. R⁴-CO-N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc. Synthesis methods for producing polyhydroxy fatty acid amides are found in U.S. Patent 5,194,639 issued March 16, 1993 to Connor, Scheibel and Severson incorporated herein by reference.

The subject compositions comprise from about 0.4% to about 8% nonionic surfactant selected from alkyl ethoxy alcohol surfactant, amine oxide surfactant, and polyhydroxy fatty acid amide surfactant; the subject compositions preferably comprise from about 2% to about 7%, more preferably from about 3% to about 6%, more preferably still from about 3.5% to about 5%, such nonionic surfactant. Such nonionic surfactant preferably comprises at least about 50%, more preferably at least about 80%, more preferably still about 100%, alkyl ethoxy ether surfactant. Preferably the weight ratio of the nonionic surfactant to HAQA cationic surfactant is greater than about 2, more preferably greater than about 4, and even more preferably greater than about 5, and most preferably greater than about 6.

The subject compositions preferably include only, or substantially only, the surfactants disclosed hereinabove, such that the surfactant system of the subject compositions preferably consists essentially of, or consists of, anionic surfactant selected from the group consisting of alkylbenzene sulfonate, alkyl sulfate and

AES surfactant (more preferably alkylbenzene sulfonate surfactant); HAQA surfactant; and nonionic surfactant selected from the group consisting of AE surfactant, amine oxide surfactant, and polyhydroxy fatty acid amide surfactant (more preferably AE surfactant).

Polymeric Soil Release Agent

Polymeric soil release agent, hereinafter "SRA" is included in the subject detergent compositions which comprise from about 0.05% to about 4%, preferably from about 0.06% to about 1.5%, more preferably from about 0.08% to about 0.7%, also preferably from about 0.16% to about 0.4%, also preferably from about 0.07% to about 0.14%, SRA.

SRA typically has hydrophilic segments to hydrophilize the surface of hydrophobic fibers such as polyester and nylon, and hydrophobic segments to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles, thereby serving as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment of fabric with SRA to be more easily cleaned in later washing of the fabric.

SRA useful in the subject invention compositions is disclosed in U.S. Patent No. 5,415,807 issued to Gosselink, Pan, Kellett and Hall on May 16, 1995, incorporated herein by reference. SRA encompasses composition mixtures comprising oligomeric, substantially linear, sulfonated poly-ethoxy/propoxy end-capped esters and crystallization-reducing stabilizers.

The esters employed comprise oxyethyleneoxy units and terephthaloyl units. Preferred esters additionally comprise units of oxy-1,2-propyleneoxy, sulfoisophthalate and, optionally, poly(oxyethylene)oxy units with degree of polymerization from 2 to 4. The SRA useful herein is a mixture of such esters with reaction by-products, crystallization-reducing stabilizers, and the like, wherein the SRA contains from about 10% to about 99.5% of said linear end-capped esters, preferably from about 25% to about 97% more preferably from about 50% to about 94%, of such esters. The esters are of relatively low molecular weight (i.e., generally below the range of fiber-forming polyesters) typically ranging from about 500 to about 8,000. Excellent SRA compositions are those wherein at least about 50% by weight of said ester has a molecular weight ranging from about 500 to about 5,000, and the SRA comprises at least about 3% of said crystallization-reducing stabilizer.

Taken in its broadest aspect, the SRA encompasses an oligomeric ester "backbone" which is end-capped on one, or preferably both, ends of the backbone by the essential end-capping units.

The essential end-capping units are anionic hydrophiles derived from sulfonated poly-ethoxy/propoxy groups and connected to the esters by an ester linkage.

Certain noncharged, hydrophobic aryldicarbonyl units are essential in the backbone unit of the oligoesters. Preferably, these are exclusively terephthaloyl units. Other noncharged, hydrophobic dicarbonyl units, such as isophthaloyl, adipoyl or the like, can also be present if desired, provided that the soil release properties of the esters (especially polyester substantivity) are not significantly diminished.

It is also possible optionally to incorporate additional hydrophilic units into the backbone units of said esters. For example, anionic hydrophilic units capable of forming two ester bonds may be used. Suitable anionic hydrophilic units of this specific type are well illustrated by sulfonated dicarbonyl units, such as sulfoisophthaloyl, i.e., $-(O)C(C_6H_3)(SO_3M)C(O)-$ wherein M is a salt-forming cation such as an alkali metal or tetraalkylammonium ion.

Generally, if it is desired to modify the units of the esters, use of additional hydrophilic units is preferable to use of additional noncharged, hydrophobic units.

Preferred esters of the SRA comprise, per mole of said ester:

- i) from about 1 to about 2 moles of sulfonated poly-ethoxy/propoxy end-capping units of the formula $(MO_3S)(CH_2)_m(CH_2CH_2O)(RO)_n-$ wherein M is a salt-forming cation such as sodium or tetraalkylammonium, m is 0 or 1, R is ethylene, propylene or a mixture thereof, and n is from 0 to 2; and mixtures thereof;
- ii) from about 0.5 to about 66 moles of units selected from the group consisting of:
 - a) oxyethyleneoxy units;
 - b) a mixture of oxyethyleneoxy and oxy-1,2-propyleneoxy units wherein said oxyethyleneoxy units are present in an oxyethyleneoxy to oxy-1,2-propyleneoxy mole ratio ranging from 0.5:1 to about 10:1; and
 - c) a mixture of a) or b) with poly(oxyethylene)oxy units wherein said poly(oxyethylene)oxy units have a degree of polymerization of from 2 to 4; provided that when said poly(oxyethylene)oxy units have a degree of polymerization of 2, the mole ratio of poly(oxyethylene)oxy units to total group ii) units ranges from 0:1 to about 0.33:1; and when said poly(oxyethylene)oxy units have a degree of polymerization of 3, the mole ratio of

poly(oxyethylene)oxy units to total group ii) units ranges from 0:1 to about 0.22:1; and when said poly(oxyethylene)oxy units have a degree of polymerization of 4, the mole ratio of poly(oxyethylene)oxy units to total group ii) units ranges from 0:1 to about 0.14:1;

- iii) from about 1.5 to about 40 moles of terephthaloyl units; and
- iv) from 0 to about 26 moles of 5-sulfoisophthaloyl units of the formula $-(O)C(C_6H_3)(SO_3M)C(O)-$ wherein M is a salt forming cation such as an alkali metal or tetraalkylammonium ion.

The preferred end-capping units of the esters are of the formula $(MO_3S)(CH_2)_m(CH_2CH_2O)(RO)_n-$ wherein M is a salt-forming cation such as sodium or tetraalkylammonium, m is 0 or 1, R is ethylene, propylene, or a mixture thereof, and n is from 0 to 2; and mixtures thereof. The end-capping units are more preferably sodium 2-(2-hydroxyethoxy)ethanesulfonate. Preferred end-capped esters are essentially in the doubly end-capped form, comprising about 2 moles of said end-capping units per mole of said ester.

The ester "backbone" of the soil release agent, by definition, comprises all the units other than the end-capping units; all the units incorporated into the esters being interconnected by means of ester bonds. Preferably, in embodiments wherein the ester backbones comprise only terephthaloyl units and oxyethyleneoxy units, the terephthaloyl units iii) ranges from about 1 to about 10 moles per ester. In preferred embodiments incorporating oxy-1,2-propyleneoxy units, the ester backbone comprises terephthaloyl units, oxyethyleneoxy, and oxy-1,2-propyleneoxy units; the mole ratio of the latter two types of unit ranging from 0.5:1 to about 10:1.

In still other highly preferred embodiments, hydrophilic units such as 5-sulfoisophthaloyl are present in the backbone and generally comprise from about 0.05 to about 26 moles per mole of said ester.

The poly(oxyethylene)oxy units, which aid in the rate of dissolution of the ester, typically constitute from 0 to about 25 mole percent of total oxyalkyleneoxy units per ester depending upon the degree of polymerization of the poly(oxyethylene)oxy units and the length of the ester backbone.

The subject SRA is well illustrated by one comprising at least about 25% ester having the empirical formula:



wherein (CAP) represents the sodium salt form of said end-capping units i); (EG/PG) represents said oxyethyleneoxy, oxy-1,2-propyleneoxy, and

poly(oxyethylene)oxy units ii); (T) represents said terephthaloyl units iii); x is from about 1 to 2; y is from about 0.5 to about 7; z is from about 1.5 to about 7; wherein x, y, and z represent the average number of moles of the corresponding units per mole of said ester. More preferably in esters of this type, the oxyethyleneoxy:oxy-1,2-propyleneoxy mole ratio ranges from about 1:1 to about 10:1; x is about 2, y is from about 1 to about 6, and z is from about 2 to about 6.

The backbone of the esters herein are preferably modified by incorporation of hydrophiles such as 5-sulfoisophthalate. A preferred SRA comprises at least about 25% ester having the empirical formula:



wherein (CAP), (EG/PG), and (T) are as defined above and (SIP) represents the sodium salt form of said 5-sulfoisophthaloyl units iv); x is from about 1 to 2; y is from about 0.5 to about 66; z is from about 1.5 to about 40; q is from about 0.05 to about 26; the oxyethyleneoxy:oxy-1,2-propyleneoxy mole ratio ranges from about 0.5:1 to about 10:1; wherein x, y, z and q represent the average number of moles of the corresponding units per mole of said ester. More preferably in esters of this type, EG:PG is from about 1:1 to about 5:1, x is about 2, y is from about 3 to about 18, z is from about 3 to about 15, and q is from about 0.5 to about 4; more preferably still x is about 2, y is about 5, z is about 5, and q is about 1.

The SRA also comprises certain crystallization-reducing stabilizers selected from the group consisting of:

- 1) sulfonate-type hydrotrope selected from the group consisting of:
 - a) $(R^1)_nAr-SO_3M$;
 - b) $(R^2)Ar(SO_3M)-O-(R^2)Ar(SO_3M)$; and
 - c) mixtures thereof;

wherein Ar is an aromatic hydrocarbon group, preferably phenyl, each R^1 is hydrogen or a C_1 - C_4 alkyl group, each R^2 is a C_1 - C_{18} alkyl group, n is from 0 to 3, and M is an alkali metal or tetraalkylammonium ion;

- 2) alkali metal and tetraalkylammonium salts of linear and branched alkylbenzenesulfonate wherein the alkyl group is from about C_5 to about C_{16} , preferably from about C_{10} to about C_{14} ;
- 3) alkyl chain sulfonate including paraffin sulfonate and other thermally-stable alkyl sulfonate variations, such as olefin sulfonate and beta-alkoxysulfonate, with about 4 to about 20 carbon atoms, provided the alkyl sulfonate is substantially free of substituents capable of entering

into esterification/transesterification reactions under the conditions used for forming the soil release agent; and

4) mixtures thereof.

The stabilizers can be integrated into the soil release agent to reduce the substantial difficulties attributable to undesirable crystallization of the oligomer during preparation and/or after introduction into the wash liquor. Oligomers with high ratios of oxyethyleneoxy to oxy-1,2-propyleneoxy units (EG/PG) in the backbone structure are especially susceptible to crystallization.

The SRA preferably comprises, in addition to the ester, from about 0.5% to about 20% of crystallization-reducing stabilizer selected from sulfonate-type hydrotrope, alkylbenzenesulfonate, paraffin sulfonate, and mixtures thereof. Preferred SRA comprises from about 3% to about 18%, more preferably from about 6% to about 15%, more preferably still from about 9% to about 13% of said stabilizers.

A preferred SRA having an oligomer with empirical formula $(CAP)_2(EG/PG)_5(T)_5(SIP)_1$ with 12% linear sodium dodecylbenzenesulfonate as a stabilizer, designated SRA-1 herein, is made as described in Example V of U.S. 5,415,807, columns 19-20. Therein an ester composition is made from sodium 2-(2-hydroxyethoxy)-ethanesulfonate, dimethyl terephthalate, dimethyl 5-sulfoisophthalate sodium salt, ethylene glycol and propylene glycol, with the integration of 12% of linear sodium dodecylbenzenesulfonate as a stabilizer. The ratio of ethylene glycol to propylene glycol incorporated in the oligomer is 2:1:1.

To a 250 ml, three neck, round bottom flask equipped with a magnetic stirring bar, modified Claisen head, condenser (set for distillation), thermometer, and temperature controller (THERM-O-WATCH® , I²R) is added sodium 2-(2-hydroxyethoxy)ethanesulfonate (18.4 g, 0.096 mol)(prepared as in Example I of U.S. Patent 5,415,807), dimethyl terephthalate (Aldrich, 46.5 g, 0.240 mol), dimethyl 5-sulfoisophthalate sodium salt (Aldrich, 14.2 g, 0.048 mol), ethylene glycol (Baker, 89.2 g, 1.44 mol), propylene glycol (Baker, 109.4 g, 1.44 mol), hydrated monobutyl-tin oxide (M&T Chemicals, 0.47 g, 2% of total reaction weight), sodium acetate (MCB, 0.89 g, 2 mol % of dimethyl 5-sulfoisophthalate, sodium salt), SIPONATE LDS-10® (Alcolac, linear sodium dodecylbenzenesulfonate, 10.0 g, vacuum dried, 12% of final oligomer weight), and silicone oil (DOW-710®, 0.08 g, 0.1% of final oligomer weight). This mixture is heated to 180°C and maintained at that temperature overnight under argon as methanol and water distill from the reaction vessel. The material is transferred to a 1000 ml, single neck, round bottom flask and heated gradually over about 20

minutes to 240°C in a Kugelrohr apparatus (Aldrich) at about 0.5 mm Hg and maintained there for 5 hours. The reaction flask is then allowed to air cool quite rapidly to near room temperature under vacuum (approximately 30 minutes). The reaction affords 56 g of the desired oligomer as an opaque, green solid.

Other Components

The compositions of the subject invention comprise from about 81% to about 94%, preferably from about 84% to about 92%, more preferably from about 86% to about 90%, other components commonly used in laundry detergent products. A typical listing of the classes and species of other surfactants, builders and other ingredients that may be included in the subject compositions appears in U.S. Patent No. 3,664,961, issued to Norris on May 23, 1972, incorporated herein by reference, and EP 550,652, published on April 16, 1992. The following are representative of such materials, but are not intended to be limiting.

Detergent Builders

The compositions of the subject invention optionally but preferably comprise detergent builders which assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils. The level of builder can vary widely depending upon the end use of the composition and its desired physical form.

Inorganic detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, silicates, carbonates (including bicarbonates and sesquicarbonates), and aluminosilicates. Non-phosphate builders are required in some locales.

In situations where phosphorus-based builders can be used, the various alkali metal phosphates such as the well-known sodium tripolyphosphates (STPP), sodium pyrophosphate (TSPP) and sodium orthophosphate can be used; STPP and TSPP are preferred, especially STPP. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030, 3,422,021; 3,400,148 and 3,422,137) can also be used.

Examples of silicate builders are the alkali metal silicates, particularly those having a $\text{SiO}_2\text{:Na}_2\text{O}$ ratio in the range of about 1.6:1 to about 3.2:1, preferably about 1.6:1; and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to Rieck. Other silicates may also

be useful, such as, for example, magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Examples of carbonate builders are the alkali metal carbonates and bicarbonates. Preferred is sodium carbonate.

Aluminosilicate builders are useful in the subject compositions. Aluminosilicate builders are of great importance in many currently marketed granular detergent compositions. Aluminosilicate builders include those having the empirical formula: $M_z(zAlO_2)_y \cdot vH_2O$ wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and v is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel et al., issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula: $Na_{12}((AlO_2)_{12}(SiO_2)_{12}) \cdot vH_2O$ wherein v is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (v = about 0 - 10) may also be used. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the subject compositions include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Preferred polycarboxylate builders include citrates, succinates, and oxydisuccinates. Polycarboxylate builders can generally be added to the compositions in acid form, but can also be added in the form of neutralized salts, such as sodium.

The compositions of the subject invention comprise from 0% to about 80% builders, preferably from about 10% to about 70%, more preferably from about 20% to about 60%, more preferably still from about 30% to about 50%. The subject compositions preferably comprise from about 5% to about 40%, more preferably from about 10% to about 30%, more preferably still from about 15% to about 25%, STPP. The subject compositions preferably comprise from about 2% to about 30% sodium carbonate, more preferably from about 5% to about 25%,

more preferably still from about 10% to about 20%. The subject compositions preferably comprise from 0% to about 15% silicates, more preferably from about 3% to about 10%, more preferably still from about 5% to about 8%.

Chelating Agent

The subject detergent compositions may also optionally contain one or more iron and/or manganese chelating agent. Such chelating agent can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates. This agent is also useful in stabilizing bleaching components of the subject compositions.

Amino carboxylates useful as optional chelating agents include ethylenediamine tetraacetates, N-hydroxyethylethylenediamine triacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraamine hexaacetates, diethylenetriamine pentaacetates, and ethanoldiglycines; alkali metal, ammonium, and substituted ammonium salts thereof; and mixtures thereof.

Amino phosphonates are also suitable for use as chelating agents in the subject compositions, when at least low levels of total phosphorus are permitted in detergent compositions. Preferably, these amino phosphonates do not contain alkanyl or alkenyl groups with more than about 6 carbon atoms. Preferred amino phosphonates are diethylenetriamine penta(methylene phosphonic acid), ethylenediamine tetra(methylene phosphonic acid), and mixtures and salts and complexes thereof. Particularly preferred are sodium, zinc, magnesium, and aluminum salts and complexes thereof, and mixtures thereof. Preferably such salts or complexes have a molar ratio of metal ion to chelant molecule of at least about 1:1, preferably at least about 2:1.

Such chelating agent can be included in the subject compositions at a level of from 0% to about 5%, preferably from about 0.1% to about 2%, more preferably from about 0.2% to about 1%, more preferably still from about 0.3% to about 0.5%.

Magnesium sulfate can optionally be included in the subject compositions as a stabilizer for the above chelating agents. It is included at a level of from 0% to about 4%, preferably from about 0.5% to about 2%.

Polymeric Dispersing Agent

The subject compositions preferably comprise polymeric dispersing agent. Suitable polymeric dispersing agent includes polymeric polycarboxylates and

polyethylene glycols, although others known in the art can also be used. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agent enhances overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylate) by crystal growth inhibition, particulate soil release peptization, and anti-redeposition.

Polymeric polycarboxylate material can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalononic acid. The presence in the polymeric polycarboxylate of monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylate can be derived from acrylic acid. Such acrylic acid-based polymer which is useful is the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymer in the acid form preferably ranges from about 2,000 to about 10,000, more preferably from about 4,000 to about 7,000 and most preferably from about 4,000 to about 5,000. Water-soluble salts of such acrylic acid polymer can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylate of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued March 7, 1967.

Acrylic/maleic-based copolymer may also be used as a preferred component of the dispersing agent. Such material includes the water-soluble salts of copolymer of acrylic acid and maleic acid (or maleic anhydride). The average molecular weight of such copolymer in the acid form preferably ranges from about 2,000 to about 100,000, more preferably from about 4,000 to about 80,000, most preferably from about 7,000 to about 65,000. The ratio of acrylate to maleate segments in such copolymer will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to about 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymer can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymer of this type is known material which is described in European Patent Application 066 915, published December 15, 1982, as well as in EP 193 360, published September 3,

1986, which also describes such polymer comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such material is also disclosed in EP 193 360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight range for this purpose ranges from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

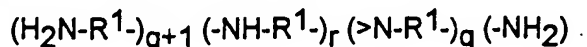
Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have an average molecular weight of about 10,000.

Another type of preferred dispersing agent includes carboxymethylcellulose (CMC) material. Such material is well-known in the art.

The above polymeric dispersing agent, if included, is typically at a level from 0% to about 7%, preferably from about 0.5% to about 3%, more preferably from about 1% to about 2.5%. Polyacrylate and acrylic/maleic copolymer dispersing agent is preferably included in the subject compositions at a level of from about 0.5% to about 3%, more preferably from about 1% to about 2%. A CMC-type dispersing agent is preferably included in the subject compositions at a level of from about 0.1% to about 1%, more preferably from about 0.2% to about 0.5%.

Another optional ingredient in the subject compositions is a soil dispersing agent which is a water soluble or dispersible alkoxylated polyalkyleneamine material. Such material can be included in the subject compositions at a level from 0% to about 1%, preferably from about 0.1% to about 0.8%, more preferably from about 0.3% to about 0.5%.

The alkoxylated polyalkyleneamine material has a polyalkyleneamine backbone of amine units having the general formula:



wherein:

- (i) each (H_2N-R^1-) unit is bonded to $(-NH-R^1-)$ or $(>N-R^1-)$;
- (ii) each $(-NH-R^1-)$ unit is bonded to any two units, provided that each is bonded to no more than one of (H_2N-R^1-) and $(-NH_2)$;
- (iii) each $(>N-R^1-)$ unit is bonded to any three units, provided that each is bonded to no more than two of (H_2N-R^1-) and $(-NH_2)$;
- (vii) the $(-NH_2)$ is bonded to $(-NH-R^1-)$ or $(>N-R^1-)$;

provided that each bond described in (i), (ii), (iii) and (iv) is between N of one unit and R¹ of another unit.

In the above general formula, q is on average from 0 to about 250, preferably from about 1 to about 100, more preferably from about 3 to about 40, more preferably still from about 5 to about 25, still more preferably from about 7 to about 15.

In the above general formula, r is on average from about 3 to about 700, preferably from about 4 to about 200, more preferably from about 6 to about 80, more preferably still from about 8 to about 50, still more preferably from about 15 to about 30.

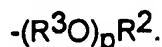
In the above general formula, the ratio q:r is preferably from 0 to about 1:4, more preferably from about 1:1.5 to about 1:2.5, more preferably still about 1:2.

In the above general formula, R¹ is linear alkanylene having from 2 to about 12 carbon atoms, preferably from 2 to about 4 carbon atoms. For preferred polyalkyleneamine backbones, less than about 50% of the R¹ moieties have more than 3 carbon atoms, more preferably less than about 25% R¹ moieties have more than 3 carbon atoms, more preferably still less than about 10% R¹ moieties have more than 3 carbon atoms. More preferred R¹ is selected from ethylene, 1,2-propylene, 1,3-propylene, and mixtures thereof. For most preferred backbones, substantially all R¹ units are the same. Most preferred R¹ is ethylene.

The polyalkyleneamine backbone described above has a molecular weight of at least about 180 daltons, preferably has a molecular weight of from about 600 to about 5000 daltons, more preferably has a molecular weight of from about 1000 to about 2500 daltons.

On the above polyalkyleneamine backbone, from about 50% to about 100% of the hydrogens bonded to the nitrogens are substituted; preferably from about 90% to about 100% of the hydrogens bonded to the nitrogens are substituted; more preferably substantially all of the hydrogens bonded to the nitrogens are substituted.

Substituents for the hydrogens bonded to the nitrogens are poly(alkyleneoxy) units having the formula



In the above formula, R³ is alkanylene having from 2 to about 6 carbon atoms, preferably from 2 to about 4 carbon atoms. R³ is preferably selected from ethylene, 1,2-propylene, and mixtures thereof. More preferably R³ is ethylene.

In the above formula, R² is selected from hydrogen, alkanyl having from 1 to about 4 carbon atoms, and mixtures thereof. Preferably R² is hydrogen.

In the above formula, p is on average from about 1 to about 50, preferably from about 3 to about 10. In general, p preferably increases with increasing molecular weight of the polyalkyleneamine backbone.

Those skilled in the art of alkoxylation of polyalkyleneamines recognize that the "degree of ethoxylation" is defined as the average number of alkoxylation per nitrogen atom substituent site and may be expressed as a fractional number. A polyalkyleneamine may have a degree of ethoxylation equal to 1 or greater and still have less than 100% of the polyalkyleneamine backbone nitrogen substituent sites substituted.

The relative proportion of primary, secondary, and tertiary amine units in the polyalkyleneamine backbone will vary, depending on the manner of preparation of the backbone.

Preferred "polyalkyleneamine backbones" herein include both polyalkyleneamine (PAA) and polyalkyleneimine (PAI); preferred backbones are polyethyleneamine (PEA) and polyethyleneimine (PEI).

PEA is obtained by a reaction involving ammonia and ethylene dichloride, followed by fractional distillation. Common PEA's include triethylenetetramine (TETA), tetraethylenepentamine (TEPA), and tetrabutylpentamine. Above pentamine, i.e., hexamine, heptamine, octamine and possibly nonamine, the cogenerically derived mixture does not readily separate by distillation and can include other materials such as cyclic amines and piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See U.S. Patent 2,792,372, Dickinson, issued May 14, 1957, incorporated herein by reference, which describes the preparation of PEA.

PEI includes the preferred polyalkyleneamine backbones useful herein. PEI can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfate, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing PEI's are disclosed in U.S. Patent 2,182,306, Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746, Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095, Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839, Crowther, issued September 17, 1957; and U.S. Patent 2,553,696, Wilson, issued May 21, 1951 (all herein incorporated by reference). In addition to the linear and branched PEI's, the compounds useful herein also include the cyclic amines that are typically formed as artifacts of synthesis. The presence of these materials may be increased or decreased depending on the conditions chosen by the formulator.

The following is a non-limiting example of the synthesis of a preferred soil dispersing agent.

Preparation of PEI 1800 E7:

"PEI 1800 E7" has a polyethyleneimine backbone having an average molecular weight of about 1800, a ratio of q:r of about 1:2, and an average degree of ethoxylation of about 7.

Ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and introduction of ethylene oxide as a liquid. A ~20 lb. net weight cylinder of ethylene oxide is set up to deliver ethylene oxide as a liquid by pumping to the autoclave with the cylinder placed on a scale so that the weight change of the cylinder can be monitored.

A 750 g portion of PEI (Nippon Shokubai, EPOMIN SP-018® having a listed average molecular weight of 1800 and a ratio of q:r of about 1:2), equating to about 0.417 moles of polymer and 17.4 moles of nitrogen substitution sites, is added to the autoclave. The autoclave is then sealed and purged of air (by applying vacuum to minus 28" Hg followed by pressurization with nitrogen to 250 psia, then venting to atmospheric pressure). The autoclave contents are heated to 130°C while applying vacuum. After about one hour, the autoclave is charged with nitrogen to about 250 psia while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally over time while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting from any reaction exotherm. The temperature is maintained between 100 and 110°C while the total pressure is allowed to gradually increase during the course of the reaction to a maximum of about 350 psia. After a total of 750 grams of ethylene oxide has been charged to the autoclave (roughly equivalent to one mole ethylene oxide per PEI nitrogen substitution site), the temperature is increased to 110°C and the autoclave is allowed to stir for an additional hour. At this point, vacuum is applied to remove any residual unreacted ethylene oxide. (If a degree of ethoxylation of 1 was desired, the process would now proceed directly to the deodorization step below.)

Next, vacuum is continuously applied while the autoclave is cooled to about 50°C while introducing 376 g of a 25% sodium methoxide in methanol solution (1.74 moles, to achieve a 10% catalyst loading based upon PEI nitrogen substituent sites). The methoxide solution is sucked into the autoclave under vacuum and then the autoclave temperature controller setpoint is increased to

130°C. A device is used to monitor the power consumed by the agitator. The agitator power is monitored along with the temperature and pressure. Agitator power and temperature values gradually increase as methanol is removed from the autoclave and the viscosity of the mixture increases and stabilizes in about 1 hour indicating that most of the methanol has been removed. The mixture is further heated and agitated under vacuum for an additional 30 minutes.

Vacuum is removed and the autoclave is cooled to 105°C while it is being charged with nitrogen to 250 psia and then vented to atmospheric pressure. The autoclave is charged to 200 psia with nitrogen. Ethylene oxide is again added to the autoclave incrementally as before while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate while maintaining the temperature between 100 and 110°C and limiting any temperature increases due to reaction exotherm. After the addition of 4500 g of ethylene oxide (resulting in a total of 7 moles of ethylene oxide per mole of PEI nitrogen substituent site) is achieved over several hours, the temperature is increased to 110°C and the mixture stirred for an additional hour.

The reaction mixture is then collected in nitrogen purged containers and eventually transferred into a 22 L three neck round bottomed flask equipped with heating and agitation. The strong alkali catalyst is neutralized by adding 167 g methanesulfonic acid (1.74 moles). The reaction mixture is then deodorized by sparging with inert gas (argon or nitrogen) through a gas dispersion frit and through the reaction mixture for about 1½ hour while agitating and heating the mixture to about 100-130°C.

Enzymes

Enzymes can be included in the subject compositions for a wide variety of fabric laundering purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and for the prevention of refugee dye transfer, and for fabric restoration. The enzymes which may be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures of two or more thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability in the presence of active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

The subject compositions typically comprise from 0% to about 5%, preferably from about 0.1% to about 2%, more preferably about 0.5% to about 1.5%, of commercial enzyme preparations.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE®. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE® and SAVINASE® by Novo Industries A/S (Denmark) and MAXATASE® by International Bio-Synthetics, Inc. (The Netherlands).

Protease enzymes in commercial preparations are included in the subject compositions at levels sufficient to provide from about 0.004 to about 2 Anson units (AU) of activity per gram of the compositions, preferably from about 0.006 to about 0.1 AU, also from about 0.005 to about 0.02 AU.

Amylases include, for example, α -amylases described in British Patent Specification No. 1,296,839 (Novo), RAPIDASE®, International Bio-Synthetics, Inc. and TERMAMYL®, Novo Industries. Amylase is preferably included in the subject compositions such that the activity of the amylase is from about 0.02 KNU to about 5 KNU per gram of the composition, more preferably from about 0.1 KNU to about 2 KNU, more preferably still from about 0.3 KNU to about 1 KNU. (KNU is a unit of activity used commercially by Novo Ind.)

The cellulases usable in the subject compositions include both bacterial and fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Cellulases disclosed in PCT Patent Application No. WO 91/17243, such as CAREZYME® (Novo), are especially useful cellulases.

Cellulase is preferably included in the subject compositions such that the activity of the cellulase is from about 0.1 CEVU to about 20 CEVU per gram of the composition, more preferably from about 1 CEVU to about 10 CEVU, more preferably still from about 2 CEVU to about 5 CEVU. (The activity of a cellulase material (CEVU) is determined from the viscosity decrease of a standard CMC solution as follows. A substrate solution is prepared which contains 35g/l CMC (Hercules 7 LFD) in 0.1 M tris buffer at pH 9.0. The cellulase sample to be analyzed is dissolved in the same buffer. 10ml substrate solution and 0.5ml enzyme solution are mixed and transferred to a viscosimeter (e.g., Haake VT 181,

NV sensor, 181 rpm), thermostated at 40°C. Viscosity readings are taken as soon as possibly after mixing and again 30 minutes later. The activity of a cellulase solution that reduces the viscosity of the substrate solution to one half under these conditions is defined as 1 CEVU/liter.)

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. The LIPOLASE® enzyme derived from *Humicola lanuginosa* and commercially available from Novo (see also EP 341 947) is a preferred lipase.

Lipase is preferably included in the subject compositions such that the activity of the lipase is from about 0.001 KLU to about 1 KLU per gram of the composition, more preferably from about 0.01 KLU to about 0.5 KLU, more preferably still from about 0.02 KLU to about 0.1 KLU. (KLU is a unit of activity used commercially by Novo Ind.)

Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution.

A wide range of enzyme materials and means for their incorporation into synthetic detergent compositions are also disclosed in U.S. Patent 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al., issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985.

Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. Patent 3,600,319, issued August 17, 1971 to Gedge et al., and European Patent Application No. 199 405, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. 3,519,570.

Bleaching Compounds - Bleaching Agents and Bleach Activators

The subject detergent compositions may optionally contain bleaching agent or a bleaching composition containing a bleaching agent and one or more bleach activator. Bleaching agent typically is at a level from 0% to about 25%, preferably from about 5% to about 20%, of the subject compositions. The amount of bleach activator typically is from 0% to about 10%, preferably from about 0.5% to about 5% of the subject compositions.

The bleaching agent can be any of the bleaching agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning

purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) can be used. A preferred level of perborate bleach in the subject composition is from about 5% to about 20%, more preferably from about 10% to about 16%.

Another category of bleaching agent that can be used encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid, diperoxydodecanedioic acid, and 6-nonylamino-6-oxoperoxycaproic acid.

Other peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE®, manufactured commercially by DuPont) can also be used.

Mixtures of bleaching agents can also be used.

Peroxygen bleaching agent, (perborate, percarbonate, etc.), is preferably combined with a bleach activator, which leads to the *in situ* production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various non limiting examples of activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al., and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylenediamine (TAED) activators are typical, and mixtures thereof can also be used. A preferred level of NOBS or TAED bleach activator in the subject compositions is from about 0.5% to about 5%, more preferably from about 0.8% to about 3%, more preferably still from about 1.2% to about 2.5%.

Fabric Softening Clay

A preferred fabric softening clay is a smectite-type clay. The smectite-type clays can be described as expandable, three-layer clays; i.e., alumino-silicates and magnesium silicates, having an ion exchange capacity of at least about 50 meq/100 g of clay. Preferably the clay particles are of a size that they cannot be perceived tactilely, so as not to have a gritty feel on the treated fabric of the clothes. The fabric softening clay, if any is desired, can be included in the subject invention compositions at levels of from about 0.1% to about 20%, preferably from about 0.2% to about 15%; more preferably from about 0.3% to about 10%.

While any of the smectite-type clays are useful in the subject invention compositions, certain clays are preferred. For example, Gelwhite GP is an

extremely white form of smectite-type clay and is therefore preferred when formulating white detergent compositions. Volclay BC, which is a smectite-type clay mineral containing at least 3% iron (expressed as Fe_2O_3) in the crystal lattice, and which has a very high ion exchange capacity, is one of the most efficient and effective clays for use in the instant compositions from the standpoint of product performance. On the other hand, certain smectite-type clays are sufficiently contaminated by other silicate minerals that their ion exchange capacities fall below the requisite range; such clays are not preferred in the subject compositions.

Clay Flocculating Agent

It has been found that the use of a clay flocculating agent in a composition containing softening clay provides improved softening clay deposition onto the clothes which results in better clothes softening performance, compared to that of compositions comprising softening clay alone. The polymeric clay flocculating agent is selected to provide improved deposition of the fabric softening clay. Typically such materials have a high molecular weight, greater than about 100,000. Examples of such materials can include long chain polymers and copolymers derived from monomers such as ethylene oxide, acrylamide, acrylic acid, dimethylamino ethyl methacrylate, vinyl alcohol, vinyl pyrrolidone, and ethylene imine. Gums, like guar gums, are suitable as well. The preferred clay flocculating agent is a poly(ethylene oxide) polymer. The amount of clay flocculating agent included in the subject compositions, if any, is about 0.2%-2%, preferably about 0.5%-1%.

Dye Transfer Inhibiting Ingredient

Another optional component in the subject compositions is a dye transfer inhibiting (DTI) ingredient to prevent diminishing of color fidelity and intensity in fabrics. A preferred polymeric DTI material is capable of binding fugitive dyes to prevent them from depositing on the fabrics. Non-limiting examples of polymeric DTI materials include polyvinylpyrrolidone N-oxide, polyvinylpyrrolidone (PVP), PVP-polyvinylimidazole copolymer, and mixtures thereof. Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as "PVPI") are also preferred. The amount of DTI included in the subject compositions, if any, is about 0.05%-5%, preferably about 0.2%-2%.

Photobleach

A preferred optional component of the subject invention composition is a photobleach material, particularly phthalocyanine photobleaches which are described in U.S. Patent 4,033,718 issued July 5, 1977, incorporated herein by

reference. Preferred photobleach is a metal phthalocyanine compound, the metal preferably having a valance of +2 or +3; zinc and aluminum are preferred metals. Such photobleach is available, for example, under the tradename TINOLUS. Zinc phthalocyanine sulfonate is available commercially under the tradename QUANTUM® from Ciba Geigy. The photobleach component, if included, is typically in the subject compositions at a level from 0% to about 0.02%, preferably from about 0.001% to about 0.01%.

Filler

Sodium sulfate and calcium carbonate are well known and often used as filler components of the subject compositions. Filler also includes minerals, such as talc and hydrated magnesium silicate-containing minerals, where the silicate is mixed with other minerals, e.g., old mother rocks such as dolomite. Sodium sulfate is a preferred filler material. Filler material is typically at a level from 0% to about 60%, preferably from about 15% to about 40%, more preferably from about 20% to about 35%.

Optical Brightener

Any optical brightener or other brightening or whitening agent known in the art can be incorporated into the subject detergent compositions. Commercial optical brighteners which may be useful can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanine, dibenzothiophene-5,5-dioxide, azole, 5- and 6-membered ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Product and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982). Anionic brighteners are preferred.

Specific examples of optical brighteners which are useful in the subject compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners include the PHORWHITE® series of brighteners from Verona. Other brighteners disclosed in this reference include: TINOPAL UNPA®, TINOPAL CBS® and TINOPAL 5BM®, TINOPAL AMS-GX®, available from Ciba-Geigy; ARTIC WHITE CC® and ARTIC WHITE CWD®, available from Hilton-Davis, located in Italy; the 2-(4-styryl-phenyl)-2H-naphthol[1,2-d]triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethylamino coumarin; 1,2-bis(-benzimidazol-2-yl)ethylene; 1,3-diphenylphrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styryl-naphth-[1,2-d]oxazole; and

2-(stilbene-4-yl)-2H-naphtho-[1,2-d]triazole. See also U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton.

Preferred brighteners also include 4,4'-bis((4-anilino-6-bis(2-hydroxyethyl)-amino-1,3,5-triazin-2-yl)amino)stilbene-2,2'-disulfonic acid disodium salt, 4-4'-bis(2-sulfostyryl)biphenyl and 4,4'-bis((4-anilino-6-morpholino-1,3,5-triazin-2-yl)-amino)stilbene-2,2'-disulfonic acid disodium salt.

Such optical brightener, or mixtures thereof, is typically at a level in the compositions from 0% to about 1%, preferably about 0.01%-0.3%.

Suds Suppressor

Compounds for reducing or suppressing the formation of suds can be incorporated into the compositions of the subject invention. A wide variety of materials may be used as suds suppressors. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979).

A preferred category of suds suppressor comprises silicone suds suppressors. This category includes polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al; U.S. Patent 3,933,672, Bartolotta et al; U.S. Patent 4,652,392, Baginski et al, issued March 24, 1987; and European Patent Application No. 89307851.9, published February 7, 1990. An exemplary silicone based suds suppressor, designated SS-1 herein, is polydimethylsiloxane with trimethylsilyl end blocking units available from Dow Corning.

The subject compositions comprise from 0% to about 1%, preferably from about 0.05% to about 0.1% suds suppressor.

Auxiliary Surfactant

The compositions of the subject invention can contain optional surfactants commonly used in detergent products. Typical listings of the classes and species of such surfactants, e.g., anionic, nonionic, zwitterionic, and amphoteric surfactants appear in U.S. 3,664,961, U.S. 3,929,678, U.S. 4,844,821, and EP 550,652. Such auxiliary surfactants may include C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the ethoxy_{1.5} carboxylates) C₁₀-C₁₈ glycerol ethers, C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, and C₁₂-C₁₈ α -sulfonated fatty acid esters. Such auxiliary surfactants may

include one or more of C₆-C₁₂ alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxylates/propoxylates), and C₁₂-C₁₈ betaines and sulfobetaines (sultaines). Conventional C₁₀-C₂₀ fatty acid soaps are also possible auxiliary surfactants. Such auxiliary surfactant is preferably not present, but can be included at a level from 0% to a total of about 5%, also about 0.5-2%.

Water

The granular compositions of the subject invention typically comprise from about 2% to about 15% water, preferably from about 4% to about 12% water, more preferably from about 5% to about 10% water.

Miscellaneous

Dyes, pigments, germicides, perfumes, glycerine, sodium hydroxide, alkylbenzene, fatty alcohol, and other minors, some of which are impurities carried in from surfactant-making processes, can also be incorporated in the subject compositions. If included, such other material is typically at a level from 0% to about 3%.

Examples

The following exemplify compositions of the subject invention, but are not intended to be limitations of the scope of the subject invention. The examples are granular detergents which may be made by well-known processes, such as spray drying of a paste or slurry, and agglomerating or dry blending in mixers.

The following list of components are utilized in the examples.

LAS: linear C₁₁-C₁₃ alkylbenzene sulfonate, sodium salt.

HDQA: linear C₁₂-C₁₄ dimethyl hydroxyethyl quaternary ammonium chloride.

AE: linear C₁₄-C₁₅ ethoxy (7) alcohol.

STPP: sodium tripolyphosphate.

Silicate: sodium silicate having a SiO₂:Na₂O ratio of 1.6.

Carbonate: sodium carbonate.

DTPA: diethylenetriamine pentaacetate, sodium salt.

DTPMP: diethylenetriamine penta(methylene phosphonic acid).

A/M copolymer: copolymer of acrylic and maleic acids, designated SOKALAN HP-22® from BASF.

CMC: carboxymethyl cellulose having an average molecular weight of 63,000.

SRA-1: polymeric soil release agent described hereinabove.

Protease: protease enzyme product designated SAVINASE 13T® from Novo Industries.

Amylase: amylase enzyme product designated 120T from Novo Industries.

Cellulase: cellulase enzyme product designated CAREZYME 5T® from Novo Industries, having an activity of 5000 CEVU/g.

Lipase: lipase enzyme product designated LIPOLASE 100T® from Novo Industries.

Perborate: sodium perborate monohydrate or tetrahydrate.

TAED: tetraacetyl ethylenediamine.

ZPS: zinc phthalocyanine sulfonate, designated QUANTUM®, from Ciba Geigy.

MgSO₄: magnesium sulfate.

Brightener: stilbene disulfonate, designated BLANKOPHOR DML®, from Miles Laboratories.

SS-1: polydimethylsiloxane with trimethylsilyl end blocking units designated EAF-1, from Dow Corning.

Sulfate: sodium sulfate.

The numbers in the following tables are weight percents.

Example

Components	1	2	3	4	5
LAS	6.9	8.0	6.9	5.99	9.73
HDQA	0.5	0.58	0.5	1.08	0.71
AE	4.5	5.4	4.5	4.28	6.39
SRA-1	0.10	0.10	0.10	0.09	0.10
STPP	19.7	19.7	19.7	18.6	19.67
Silicate	6.0	6.0	6.0	7.2	6.0
Carbonate	17.5	17.5	17.5	20	17.5
DTPA	0.39	0.39	0.39	--	0.39
DTPMP	--	--	--	0.36	--
A/M copolymer	1.59	1.59	1.59	1.50	1.59
CMC	0.29	0.29	0.29	0.26	0.29
Protease	0.32	0.32	0.57	0.31	0.32
Amylase	0.18	0.18	0.38	0.17	0.18
Cellulase	0.16	0.16	0.16	0.07	0.16
Lipase	0.095	0.095	0.095	0.08	0.095
Perborate monohydrate	10.45	10.45	--	--	10.45
Perborate tetrahydrate	--	--	15.20	--	--
TAED	1.52	1.52	2.23	1.44	1.52
ZPS	0.0015	0.0015	0.0015	0.0015	0.0015
Brightener	0.114	0.114	0.114	0.11	0.114

Perfume	0.23	0.40	0.22	0.23	0.22
MgSO ₄	1.45	1.45	1.45	0.54	1.45
SS-1	0.07	0.08	0.07	0.07	0.09
Moisture	9	9	9	7.2	9
Sulfate	balance	balance	balance	balance	balance

Example

Components	6	7	8	9
LAS	7.5	7.5	7.5	7.5
HDQA	0.5	1.0	0.5	1.0
AE	0.5	0.5	4.0	4.0
SRA-1	0.2	0.2	0.2	0.2
STPP	13	13	13	13
Silicate	6.5	6.5	6.5	6.5
Carbonate	4.0	4.0	4.0	4.0
A/M copolymer	0.06	0.06	0.06	0.06
CMC	0.12	0.12	0.12	0.12
ZPS	0.0045	0.0045	0.0045	0.0045
Perfume	0.25	0.25	0.25	0.25
Moisture	5.3	5.3	5.3	5.3
Sulfate	balance	balance	balance	balance

The subject invention includes processes for laundering fabrics using the compositions described hereinabove. Preferred processes are machine washing operations using such compositions.

The subject processes include incorporating the subject compositions in water, typically at concentrations of from about 3000 ppm to about 8000 ppm, preferably from about 4000 ppm to about 7000 ppm, more preferably from about 5000 ppm to about 6000 ppm, in which fabrics are washed. The subject washing operations preferably are carried out at wash solution temperatures of from about 10°C to about 90°C, more preferably from about 12°C to about 70°C, for a period of from about 10 min to about 60 min, more preferably from about 15 min to about 40 min. The subject wash solutions are preferably within the pH range of from about 9.5 to about 10.8, more preferably from about 10.0 to about 10.5.

While particular embodiments of the subject invention have been described hereinabove, it will be obvious to those skilled in the art that various changes and modifications to the subject invention can be made without departing

from the spirit and scope of the invention. It is intended to cover, in the appended claims, all such modifications that are within the scope of this invention.

1. A detergent composition comprising:

a) from 6% to 18% surfactant, the composition comprising:

- 1) from 5% to 10% anionic surfactant selected from alkylbenzene sulfonate surfactant, alkyl sulfate surfactant and alkyl ethoxy ether sulfate surfactant having an average of from 0.5 to 9 moles ethoxy per mole surfactant;
- 2) from 0.2% to 2% hydroxyalkyl quaternary ammonium cationic surfactant having the structure:



wherein R is long-chain alkyl, R' is short-chain alkyl, R'' is $H(OCH_2CHB)_p$, B is H or CH_3 ; n is 0 to 3, m is 0 to 3, $n + m$ is 3, p is from 0.5 to 4, p times m is from 0.5 to 4, and Z^- is a water-soluble anion; and

- 3) from 0.4% to 8% nonionic surfactant selected from alkyl ethoxy alcohol surfactant having an average of from 6 to 10 moles ethoxy per mole surfactant, amine oxide surfactant, and polyhydroxy fatty acid amide surfactant;

b) from 0.05 to 4% polymeric soil release agent, the soil release agent comprising:

1) from 10% to 99.5% esters comprising, per mole of said ester:

- i) from 1 to 2 moles of sulfonated poly-ethoxy/propoxy end-capping units (CAP) of the formula $(MO_3S)(CH_2)_m(CH_2CH_2O)(RO)_n$ wherein M is a salt-forming cation, m is 0 or 1, R is ethylene, propylene or a mixture thereof, and n is from 0 to 2; and mixtures thereof;

- ii) from 0.5 to 66 moles of units (EG/PG), comprising oxyethyleneoxy (EG) and optionally oxy-1,2-propyleneoxy (PG), selected from:

- a) oxyethyleneoxy units;
- b) a mixture of oxyethyleneoxy and oxy-1,2-propyleneoxy units having an oxyethyleneoxy to oxy-1,2-propyleneoxy mole ratio ranging from 0.5:1 to 10:1; and
- c) a mixture of a) or b) with poly(oxyethylene)oxy units wherein said poly(oxyethylene)oxy units have a degree

of polymerization of from 2 to 4; provided that when said poly(oxyethylene)oxy units have a degree of polymerization of 2, the mole ratio of poly(oxyethylene)oxy units to total group ii) units ranges from 0:1 to 0.33:1; and when said poly(oxyethylene)oxy units have a degree of polymerization of 3, the mole ratio of poly(oxyethylene)oxy units to total group ii) units ranges from 0:1 to 0.22:1; and when said poly(oxyethylene)oxy units have a degree of polymerization of 4, the mole ratio of poly(oxyethylene)oxy units to total group ii) units ranges from 0:1 to 0.14:1;

- iii) from 1.5 to 40 moles of terephthaloyl units (T); and
- iv) from 0 to 26 moles of 5-sulfoisophthaloyl units (SIP) of the formula $-(O)C(C_6H_3)(SO_3M)C(O)-$ wherein M is a salt forming cation such as an alkali metal or tetraalkylammonium ion;
- 2) from 0.5% to 20% crystallization-reducing stabilizer selected from sulfonate-type hydrotrope, alkylbenzene sulfonate, paraffin sulfonate, and mixtures thereof; and
- c) from 80% to 94% other components.

2. The composition of Claim 1 wherein the weight ratio of nonionic surfactant to cationic surfactant is greater than 4.

3. A detergent composition comprising:

- a) from 6% to 18% surfactant, the composition comprising:
 - 1) from 5% to 10% anionic surfactant selected from alkylbenzene sulfonate surfactant, alkyl sulfate surfactant and alkyl ethoxy ether sulfate surfactant having an average of from 0.5 to 9 moles ethoxy per mole surfactant;
 - 2) from 0.2% to 2% hydroxyalkyl quaternary ammonium cationic surfactant having the structure:



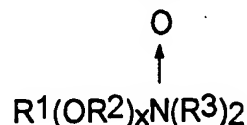
wherein R is long-chain alkyl, R' is short-chain alkyl, R'' is $H(OCH_2CH_2)_p-$, B is H or CH_3 ; n is 0 to 3, m is 0 to 3, n + m is 3, p is from 0.5 to 4, p times m is from 0.5 to 4, and Z⁻ is a water-soluble anion; and

- 3) from 0.4% to 8% nonionic surfactant selected from alkyl ethoxy alcohol surfactant having an average of from 0.5 to 25 moles ethoxy per mole surfactant, amine oxide surfactant, and polyhydroxy fatty acid amide surfactant wherein the weight ratio of nonionic surfactant to hydroxyalkyl quaternary ammonium cationic surfactant is greater than 4;
- b) from 0.05 to 4% polymeric soil release agent, the soil release agent comprising:
 - 1) from 10% to 99.5% esters comprising, per mole of said ester:
 - i) from 1 to 2 moles of sulfonated poly-ethoxy/propoxy end-capping units (CAP) of the formula $(\text{MO}_3\text{S})(\text{CH}_2)_m(\text{CH}_2\text{CH}_2\text{O})(\text{RO})_n^-$ wherein M is a salt-forming cation, m is 0 or 1, R is ethylene, propylene or a mixture thereof, and n is from 0 to 2; and mixtures thereof;
 - ii) from 0.5 to 66 moles of units (EG/PG), comprising oxyethyleneoxy (EG) and optionally oxy-1,2-propyleneoxy (PG), selected from:
 - a) oxyethyleneoxy units;
 - b) a mixture of oxyethyleneoxy and oxy-1,2-propyleneoxy units having an oxyethyleneoxy to oxy-1,2-propyleneoxy mole ratio ranging from 0.5:1 to 10:1; and
 - c) a mixture of a) or b) with poly(oxyethylene)oxy units wherein said poly(oxyethylene)oxy units have a degree of polymerization of from 2 to 4; provided that when said poly(oxyethylene)oxy units have a degree of polymerization of 2, the mole ratio of poly(oxyethylene)oxy units to total group ii) units ranges from 0:1 to 0.33:1; and when said poly(oxyethylene)oxy units have a degree of polymerization of 3, the mole ratio of poly(oxyethylene)oxy units to total group ii) units ranges from 0:1 to 0.22:1; and when said poly(oxyethylene)oxy units have a degree of polymerization of 4, the mole ratio of poly(oxyethylene)oxy units to total group ii) units ranges from 0:1 to 0.14:1;
 - iii) from 1.5 to 40 moles of terephthaloyl units (T); and

- iv) from 0 to 26 moles of 5-sulfoisophthaloyl units (SIP) of the formula $-(O)C(C_6H_3)(SO_3M)C(O)-$ wherein M is a salt forming cation such as an alkali metal or tetraalkylammonium ion;
- 2) from 0.5% to 20% crystallization-reducing stabilizer selected from sulfonate-type hydrotrope, alkylbenzene sulfonate, paraffin sulfonate, and mixtures thereof; and
- c) from 80% to 94% other components.

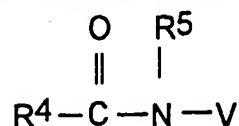
4. The composition of any of Claims 1-3 wherein:

- 1) in the structures of the anionic surfactants,
 - i) the alkylbenzene sulfonate surfactant has an alkyl with an average of from 9 to 16 carbon atoms;
 - ii) the alkyl sulfate surfactant has an alkyl with an average of from 10 to 16 carbon atoms;
 - iii) the alkyl ethoxy ether sulfate surfactant has an alkyl with an average of from 10 to 16 carbon atoms, and has from 1 to 7 moles ethoxy per mole surfactant;
- 2) in the structure of the cationic surfactant, R is alkyl having an average of from 9 to 16 carbon atoms, R' is methyl or ethyl, m is 1 or 2, n is 1 or 2, and p is 1; and,
- 3) in the structures of the nonionic surfactants,
 - i) the amine oxide surfactant has the structure:



wherein R¹ is alkyl having an average of from 10 to 18 carbon atoms, R² is an alkylene or hydroxyalkylene group with from 2 to 3 carbon atoms, x is from 0 to 3, and each R³ is alkyl or hydroxyalkyl having from 1 to 3 carbon atoms;

- ii) the polyhydroxy fatty acid amide surfactant has the structure:



wherein R⁴ is alkyl having an average of from 10 to 18 carbon atoms, R⁵ is C₁-C₆ alkyl, hydroxyalkyl, or alkyloxyalkyl, and V is a polyhydroxyhydrocarbyl moiety derived from a reducing sugar.

5. The composition of any of Claims 1-3 wherein the polymeric soil release agent comprises:
 - (1) from 25% to 97%, preferably from 50% to 94%, said esters having a molecular weight of from 500 to 8,000, preferably from 500 to 5,000, the esters having the formulation: $(CAP)_x(EG/PG)_y(T)_z(SIP)_q$, wherein the ratio EG:PG is from 1:1 to 5:1, preferably 2:1, x is 2, y is from 3 to 18 preferably 5, z is from 3 to 15, preferably 5, and q is from 0.5 to 4, preferably 1; and
 - (2) from 3% to 18%, preferably from 6% to 15%, said stabilizer, the stabilizer preferably being C₁₀-C₁₄ alkylbenzene sulfonate.
6. The composition of any of Claims 1-3 wherein the anionic surfactant comprises at least 80% said alkylbenzene sulfonate surfactant, and the nonionic surfactant comprises at least 80% said alkyl ethoxy alcohol surfactant.
7. The composition of any of Claims 1-3 wherein the composition comprises from 0.4% to 0.8%, of the cationic surfactant; and from 2% to 7% of the nonionic surfactant.
8. The composition of any of Claims 1-3 wherein the composition comprises from 8% to 15% said surfactant, from 0.08% to 1.5% said polymeric soil release agent, and from 84% to 92% other components.
9. The composition of any of Claims 1-3 wherein, in the structure of the cationic surfactant, R is alkyl having an average of from 12 to 14 carbon atoms, R' is methyl, B is H, m is 1, and n is 2.
10. The composition of any of Claims 1-3 wherein the anionic surfactant is 100% said alkylbenzene sulfonate surfactant, the alkyl having an average of from 11 to 14 carbon atoms; and the nonionic surfactant is 100% said alkyl ethoxy alcohol surfactant having an average of from 12 to 15 carbon atoms, and having from 7 to 9 moles of ethoxy per mole surfactant.

11. The composition of any of Claims 1-3 wherein the composition comprises from 10% to 14% surfactant, the surfactant consisting essentially of (weight % of the composition) from 6% to 9% said alkylbenzene sulfonate surfactant, from 0.3% to 1.2%, said hydroxyalkyl quaternary ammonium cationic surfactant, and from 3% to 6% said alkyl ethoxy alcohol surfactant; from 0.16% to 0.4% said polymeric soil release agent, and from 86% to 90% other components.